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3. ABSTRACT

This is the Yearly Report of the Novel Nanophosphors for High Efficiency Fluorescent Lamps, Department of Energy (DOE). The overall goal of this three-year program is to develop novel hybrid phosphors by coating commercially available lamp phosphors with highly stable wide band-gap nanocrystalline phosphors (NCP). The novel hybrid phosphors will increase the efficiency of the fluorescent lamps by up to 32%, enabling total energy savings of 0.26 quads, the reduction in the U.S. energy bill by $6.5 billion and the reduction of the annual carbon emission by 4.1 billion kilogram. The prime technical approach is the development of NCP quantum-splitting phosphor (QSP) and ultra-violet emitting phosphors with quantum efficiencies exceeding that of the conventional phosphors at 185 nm. Our chief achievement, during the current contract period, pertains to the successful synthesis and characterization of coated phosphors. We demonstrated several synthesis techniques for the coating of micron sized commercial phosphors with quantum-splitting and UV emitting nanophosphors. We have also continued our fundamental investigations into the physical processes that determine the quantum efficiency of the nanophosphors and this has further helped codify a set of rules for the host lattice that support efficient quantum splitting and UV emission at room temperature. In this report we summarize the technical work completed under the Program, summarize our findings about the performance limits of the various technologies we investigated, and outline promising paths for future work.

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5. INTRODUCTION

5.1 Program Goals and Benefits

The overall goal of this program was to reduce energy consumption and concurrently reduce pollution by developing novel hybrid phosphor system based on nanocrystalline quantum splitting and ultraviolet emitting phosphors with quantum efficiencies exceeding that of the conventional phosphors at 185 nm . By combining advanced phosphors and innovating system modeling for full optimization, we believe we can further increase the efficiency of fluorescent lamps with the use of quantum-splitting phosphors which, on average, produce more than one visible photon for each incident ultraviolet photon.

This Program will provide benefit to the entire lighting industry and beyond. Achievement of the project goals will save money for US end-users, while the whole country will benefit from reduced energy consumption and pollution from fossil fuel power plants. The estimated reduction in national energy consumption through use hybrid phosphor system based on quantum-splitting phosphors is 0.26 quads uin The novel hybrid phosphors will increase the efficiency of the fluorescent lamps by up to 32%, enabling total energy savings of 0.26 quads, while the estimated reduction of the annual carbon emission by 4.1 billion kilogram.

5.2 Technical Approach

Our project goals and the technical paths we have pursued area driven by our desire to closely approximate conventional fluorescent lamps in form, cost and manufacturing process. The quantum efficiency of the current fluorescent lamp phosphors is nearly 100 percent for 254 nm radiation but only about 70% for 185 nm radiation. Consequently, if there is any hope of significantly increasing the efficacy of linear fluorescent lamps we have to focus our attention to the more efficient conversion of the 185 nm radiation of the mercury discharge. To improve the conversion efficiency of the 185 nm radiation, we took into consideration the development of quantum splitting phosphors, which, on average, produce more than one visible photon for each incident ultraviolet photon. We also consider the development of efficient ultraviolet emitting phosphors, which display higher quantum efficiency under 185 nm radiation relative to the current triphosphor blend of the conventional fluorescent lamp. However, even though the quantum efficiency of the proposed quantum-splitting and the ultraviolet emitting phosphors is higher, the simple addition of these phosphors with particle size in the micrometer range to the conventional phosphor blend results in the strong scattering of the 254 nm radiation. This scattering event is detrimental to the overall lamp performance (lumen output) and the goal of the program is unattainable with large particle size of new phosphors. To realize the full benefit of the quantum splitting and ultraviolet emitting phosphors, a novel hybrid phosphor system composed of nanocrystalline quantum-splitting/ultraviolet emitting phosphors coating the highly efficient triphosphor particles must be realized. This entails the development of nanocrystalline phosphors with high

quantum efficiency under 185 nm and with size distribution that minimizes the scattering of the 254 nm radiation.

5.3 Collaborations

Several major work are formally subcontracted outside GE. The optical characterization of quantum-splitting phosphors which included the measurement of excitation and emission spectrum under vacuum ultraviolet radiation and the determination of radiative and nonradaitive transitions was subcontracted to Prof. U. Happek at the University of Georgia. Nanocerox (formally TAL Materials, Inc.) which is a recognized leader in the development of oxide nanoparticles, is subcontracted for the manufacturing of the identified nanocrystalline phosphors. Clarkson University, which is recognized leader in the handling and coating of nanocrystalline phosphors is subcontracted for the development of conformal coatings of the nanocrystalline phosphors on the micron sized conventional phosphors. Keanetech, LLC has been subcontracted for Designing and Building a Powder Generator for Continuous Synthesis and Coating of Mixed Oxide Powders by a Organic-Inorganic method.

6. RESULTS AND DISCUSSIONS

6.1 Coating of core phosphor particles by nanosized phosphors (GE GRC and Clarkson University)

The attainment of uniform coating of the nano phosphors over the micron sized phosphor particles is the major task to which we devoted the vast majority of our technical development effort. The focus for development work along the prime technical path was the trivalent praseodymium ion in an previously identified host lattice. It is noteworthy that the successful attainment of a uniform coating over the core particles requires the determination of optimum conditions of synthesis, which is usually a lengthy task because there are many independent parameters, such as (1) the temperature of precipitation (2) the rate of precipitation (3) the ratio of the reactants (4) the atmosphere and the temperature-time cycle during reaction. The attainment of a successful coating requires that a large number of samples be synthesized and tested for their quantum efficiency and absorption of 254 nm UV radiation. In this section we provide an overview of progress made in developing (synthesizing) coated "hybrid" phosphors.

Essentially the coating experiments were carried out by precipitating the nano phosphors on to the surface of the commercially available phosphors. For coating purposes, it is essential to determine the morphology of the nano particles and their state of aggregation. This is strongly dependent on the synthesis procedure. As an example, in Figure 1, we show the electron micrographs of a particular nano phosphor that have been synthesized in two different ways. It is quite evident that in the two different synthesis procedures results in different degree of particle aggregation. Particles in the electron micrograph shown on the left hand side are highly aggregated while particles on the right hand side are well dispersed. It is also evident that the morphology of the particles is that of the needle type.

Figure 1: SEM of nano particles synthesized under two different conditions. The particles on the left are highly aggregated and particles on the right are well dispersed. Note the needle like morphology of the particles.

From both the physical and chemical standpoints, the role of the interacting surfaces between the nano particles and the core particles is of considerable importance. It should be noted that the coating process may be essentially physical in nature or it may result in chemical bonding between the nano and the core particles. If the coating is physical in

nature then one must consider the electrostatic interaction between the surfaces of the particles. Hence knowledge of the Zeta potential of both the core and the nano particles is of great importance. We employed Zeta potential measurements to understand the nature of bonding between the nanoparticles and the core phosphor particles. As an example, in Figure 2 we exhibit the zeta potential of the core particle and that of the nano phosphor particles as a function of the solution pH.

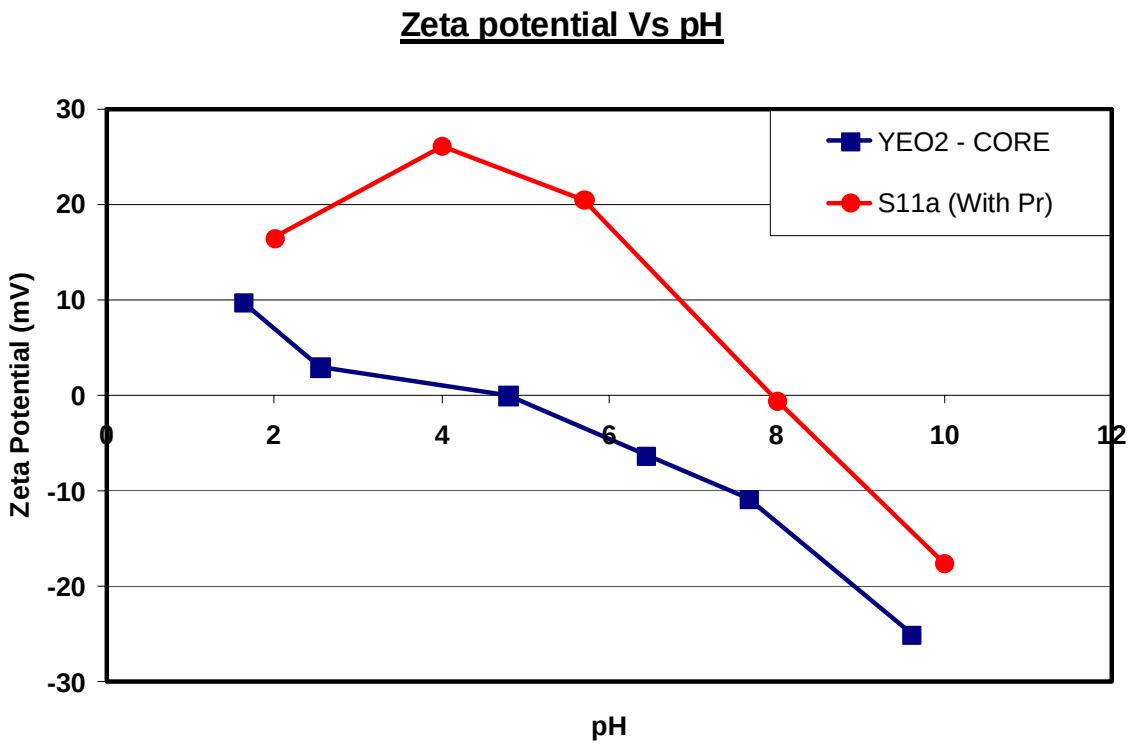

Figure 2: Zeta potential values over a range of pH for the core particle and the nano phosphor particles.

The results from the Zeta potential measurements and as exhibited in figure 2, showed that for this specific system the optimum condition for the coating experiments is at a solution pH of 6. We used both the aggregated and the well-dispersed nano particles in the coating experiments to evaluate the differences in the relative coating efficiencies. Figure 3a shows that with the well-dispersed particles a more uniform coating is attained relative to the agglomerated precursor material where the coating is rather very irregular (Figure 3b).

(a) (b)

Figure 3: Transmission electron micrograph of coated particles (a) well-dispersed precursor and (b) aggregated precursor.

The surface coating so obtained and as evidenced from the TEM of Figure 3 is very thin. The thickness of the coating layer was found to be dependent on the precipitation rate. Fast precipitation rate, which occurred when the reactants were mixed usually, gave very thin surface layer. Hence, by controlling the precipitation rate it should be possible to control the thickness of the coating layer. This involved a rather extensive study of the main interactions between the various synthesis parameters such as reactant concentration, flow rate and temperature, to name a few. The end result of this study was the development of a new controlled precipitation technique that yielded uniform and thick surface layer of the nano particles on the core particles.

The TEM of the final product obtained from the optimized proportions and method of precipitation is shown in Figure 4. It should be noted that complete covering was observed on all the particles. In general, if the samples were prepared at room temperature, the coating thickness varied from 100 to 150 nm while for samples prepared at elevated temperatures (80 C), the thickness varied from 100 nm to 200 nm. The entire coating process was completed during the first thirty minutes. Longer times did not result in thicker coating.

In order to further increase the coating thickness an attempt was made to repeat the above coating process onto a core particle that was already coated. The repetition yielded a uniform multiple nano bilayer coating on the core phosphor particles. Figure 5 shows that the coating thickness could now be increased to 200-300 nm.

Figure 4: Transmission electron micrograph of coated particles using well-dispersed precursor.

Figure 5: Transmission electron micrograph of double coated particles using well-dispersed precursor.

In the above experiments the morphology of the precursor nano particles are characterized by thin needle like structure. Although there is not a comprehensive set of data on which to base a broad statement, it seems that there may be some limitations to the extent to which the thin needle like materials may uniformly coat the core particles in an efficient manner. It is for this reason that we also investigated the coating efficiency with nano particles that are thicker and more elongated than the needle like materials.

The TEM of thicker and elongated precursor particles produced using the surfactant techniques developed within the program is shown in Figure 6. The particle size of the precursor was measured by the technique of X-ray diffraction and determined to be approximately 32 nm (Figure 7). The TEM of the coated particles using such precursor particles is exhibited in Figure 8. It is observed that a uniform and relatively strong outer coating is attained.

The quantum efficiency and the intrinsic ultra-violet (254 nm) absorption of the core particles after the coating process remained high and similar to that of the uncoated particles. This shows that the outer coating by the nano particles did not adversely influence the 254 nm reflectance. We were also successful in producing a large batch (85 grams) of the coated particles by the surfactant technique.

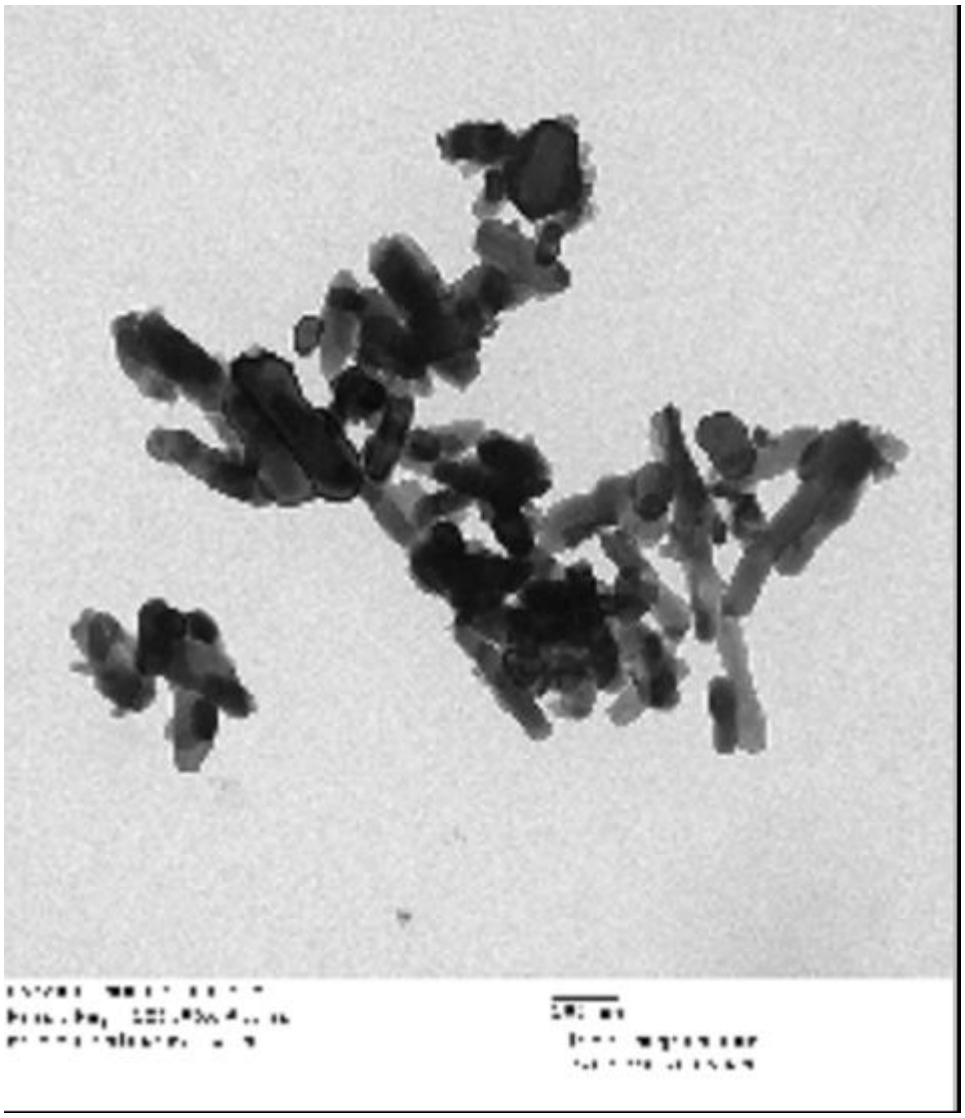

Figure 6: Transmission electron micrograph of precursor particles synthesized by a propriety technique.

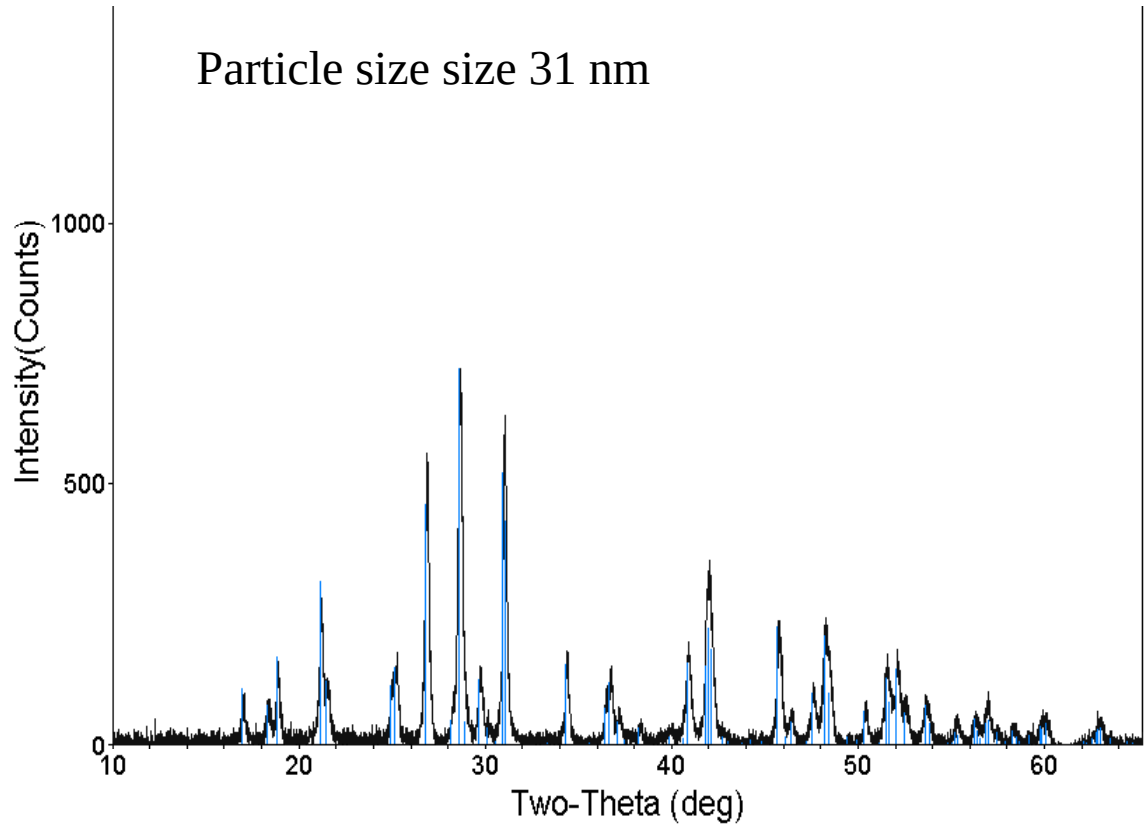

Figure 7: The X-ray diffraction pattern of the precursor material showing the attainment of particles with 31 nm particle size.

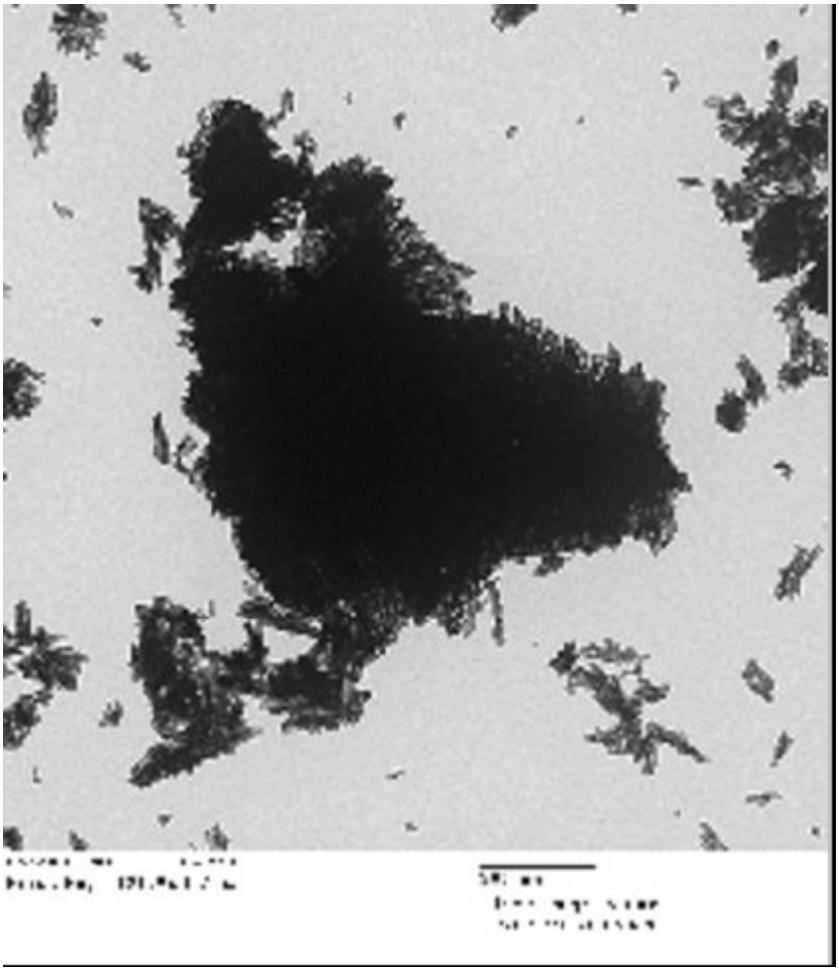

Figure 8: Transmission electron micrograph of coated core particles using precursor particles with morphology shown in Figure 6.

6.2 Summary of the results obtained from Keanetech

We briefly summarize the physical characterization work performed on the samples that were synthesized by Keanetech by their propriety method**.** Keanetech has processed coated powders of nano particles onto micronsize powders of commercial phosphors. The SEMs shown in Figure 4-Left seems to display a very homogeneous coating. Figure 9-right shows an area where two necked particles were cleaved, and shows a coating of nanoparticles of approximately 400-600nm thick. Further characterization by TEM and higher magnification SEM is currently underway. These samples will be scaled to a 50g batch that will be tested at GE Global Research (XRD, QE) and at GE CP (lamp testing). The results obtained from Keanetech are very encouraging since the work demonstrates potential manufacturing technique of these nanocrystalline phosphors.

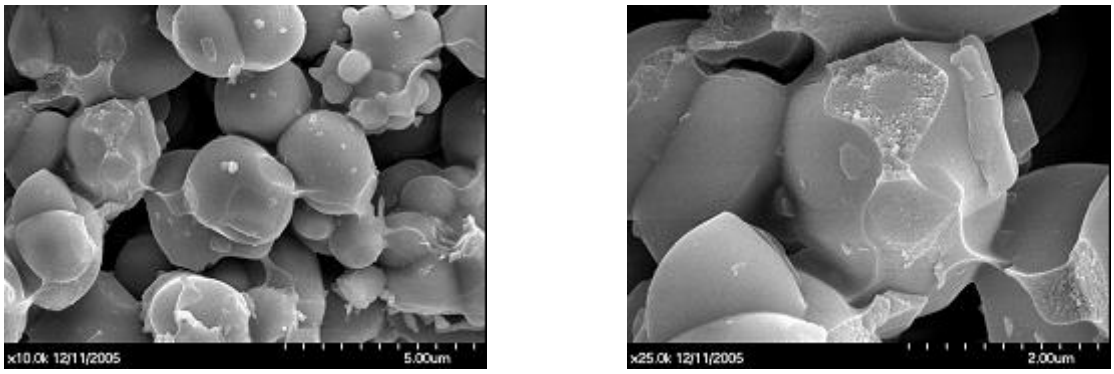

Fig. 9. SEM of coated particles showing very good coverage (Left). Cleaved surface between two coated grains, showing a 400-600nm thickness coating of nanoparticles.

6.3 Fundamental investigations on the luminescence of UV emitting and quantum-splitting phosphors

In this section we briefly summarize the fundamental investigations on the UV emitting and quantum-splitting phosphors. The focus for development work along the prime technical path was the Pr^{3+} in various oxide based host lattice materials. However, it may be reasonable to focus our attention on the luminescence processes of an efficient (i.e. a phosphor that exhibits quantum yield in excess of unity) quantum-splitting phosphor in order to gain further insights into the factors that control the efficiency of the quantum-splitting process. For this reason we choose to investigate the relative probabilities of radiative and nonradiative transitions in the well-known quantum-splitting phosphor, $YF_3:Pr^{3+}$. The maximum quantum efficiency of this phosphor approaches 160%.

In commencing a discussion of the quantum efficiency attained in a two-photon emission process, we may first enquire into the temperature dependence of the decay time and the emission intensity of the Pr^{3+} $^1S_0 \rightarrow {}^1I_6$ optical transition, which is the first step in the quantum splitting process. The probability of radiative and nonradiative rates were determined by measuring the temperature dependence of the decay time of this transition (Figure).

It may be noted that a decrease in the lifetime of the $^1S_0$ excited state is evidenced only at very high temperatures (for T> 500 K). Below T= 500 K, the decay time remains substantially constant indicating that the relative probability of energy loss by electron-phonon interactions is negligible. The lifetime quenches rapidly when the temperature is increased beyond 500 K. The activation energy involved in the quenching process is estimated by fitting the temperature dependence of the lifetime to an Arrehenius type process. The thermal activation energy required to raise the system from the radiative excited state to a higher level where the nonradiative transition to the ground state (or any other excited state) occurs is 4865 cm^{-1} (0.60 eV). It is interesting to note that this energy corresponds closely to the energy difference between the Pr^{3+} $^1S_0$ (46 500 cm^{-1}) and the lowest energy 4f5d (51 216 cm^{-1}). According to this picture, the quenching of the $^1S_0$

lifetime is attributed to the thermal excitation of the $^1S_0$ state to the 4f5d state. The fate of the excitation energy after it occupation of the 4f5d state is under investigation.

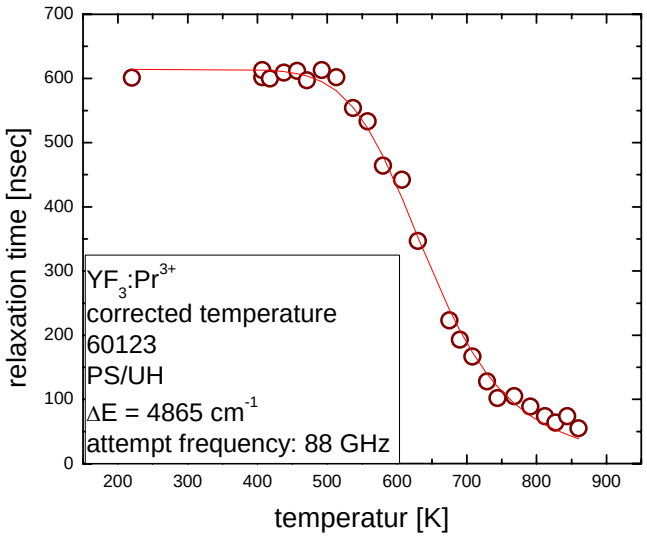

Figure 10: The temperature dependence of the $^1S_0 \rightarrow {}^1I_6$ lifetime in $YF_3:Pr^{3+}$ phosphor. The fitting gives an energy separation of 4865 cm^{-1} between the $^1S_0$ and the 4f5d states.

We have also evaluated the quality of the nanocrystals produced by our surfactant-templated-assisted route by carefully examining the photoexcitation, emission and time-resolved fluorescence decay of the Pr^{3+} ion that is incorporated in the nanocrystals. It is especially noteworthy that the quantum efficiency of the nanocrystals was determined to be equivalent to that of the micron sized materials. This is exemplified in Figure 11 which shows that the temperature dependence behavior of the $^1S_0 \rightarrow {}^1I_6$ lifetime in nanocrystalline and micron size $SrAl_{12}O_{19}:Pr^{3+}$ are equivalent. From this data alone, one can conclude that the detrimental effects of surface-induced loss mechanisms that are usually more pronounced at the nanometer particle size of the phosphors, is absent in our materials due to their high quality. The high quality of our nanocrystals is traceable to the careful optimization of the phosphor synthesis. A detailed paper on this issue has been recently published (S. Loureiro et al., Chemistry of Materials, volume 17, page 3108-3113, 2005).

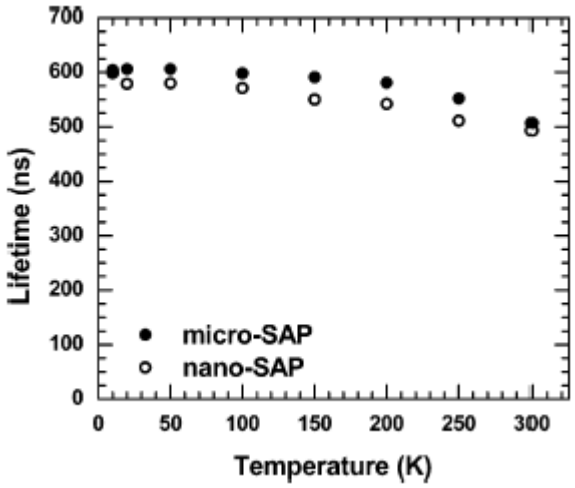

Figure 11: Temperature dependence of the $^1S_0$ relaxation time for the nanocrystalline (open circle) and microcrystalline (solid dots) $SrAl_{12}O_{19}:Pr^{3+}$ phosphor.

7. SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

This final section will be devoted to a brief summary of the status of this work and some considerations for future research and development.

From our investigations of the requirement of the particle size we conclude that the achievement of improved lamp output in the hybrid phosphor concept is only possible if the particle size of the nanocrystalline phosphor is less than 100 nm. Particles above 100nm in size increase the scattering of the 254 nm radiation.

Our work to develop coated phosphors has resulted in high quality "hybrid" phosphors with little or no loss in the intrinsic 254 nm absorption and quantum efficiency of the core particles. This implies that the scattering of the primary 254 nm radiation of the mercury discharge is minimized indicating that we have achieved a particle size of the outer coating (the nano phosphor) less than 100 nm. Further we have demonstrated that the coating procedures developed within the program attains uniform surface layers of the nano phosphors.

The final indicator of the phosphor efficiency is its performance in a fluorescent lamp. The next step in our program involves the demonstration of increased lumen output from the hybrid phosphor in fluorescent lamps. This will necessitate the synthesis of large amounts of the coated phosphor. We will examine the suspension characteristic of the hybrid phosphors, the efficiency with which they coat the surface of the fluorescent bulb and determine their 100-hour lumen output and long time (5000 hour) maintenance. We strongly recommend the continued synthesis and further characterization of the hybrid phosphors. With regards to the discovery of new phosphors we would also strongly recommend the continued exploration and refinement of the phosphor design rules that were developed within the previous DOE funded program and which were further substantiated within this program.

With regards to the manufacturability of these materials, we would strongly encourage the continued exploration and refinement in the commercial synthesis techniques that are being developed by our subcontractors

A further benefit of this program is the following. To the extent that a surface coating for the nano phosphor could protect conventional phosphors from bombardment by 185 nm radiation, one might be able to improve the lumen maintenance of conventional lamps (that is, reduce the 1-40% decrease in phosphor efficiency which occurs over the operational life of conventional fluorescent lamps). To introduce nano phosphors that absorb but are not damaged by 185nm radiation as a protective surface barrier to phosphors which degrade under 185nm radiation could allow previously unstable, but highly efficient phosphors to survive in a conventional lamp.